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Reaction of Cobalt in SO₂ Atmospheres at Elevated Temperatures

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NASA

REACTION OF COBALT IN SO_2 ATMOSPHERES AT ELEVATED TEMPERATURES

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ABSTRACT

The reaction rate of cobalt in SO_2 -argon environments has been measured at 650°, 700°, 750°, and 800° C. Product scales consist primarily of an interconnected sulfide phase in an oxide matrix. At 700° to 800° C a thin sulfide layer adjacent to the metal is also observed. At all temperatures, the rapid diffusion of cobalt outward through the interconnected sulfide appears to be important. At 650° C, the reaction rate slows dramatically after 5 min due to a change in the distribution of these sulfides. At 700° and 750° C the reaction is primarily diffusion controlled—values of $D_{\text{Co}}(\text{CoS})$ calculated from this work show favorable agreement with values of $D_{\text{Co}}(\text{CoS})$ calculated from previous sulfidation work. At 800° C a surface step becomes rate limiting.

INTRODUCTION

Metals and alloys may be exposed to complex gas environments at elevated temperatures in a variety of industrial applications. Often combustion of fossil fuels will lead to sulfur oxides which may have deleterious effects on the metal or alloy in question. Nickel and cobalt are important base metals used in turbine components. However both these metals corrode dramatically faster in SO_2 than in O_2 . For nickel at 600° C the ratio of rates is about 10^6 ; for cobalt at 750° C this ratio is about 10^3 . In this laboratory, extensive work has been done on the reaction of nickel with SO_2 and equilibrated SO_2 - O_2 mixtures (1,2). In order to determine if some of the same principles hold for the reaction of cobalt with SO_2 , similar experiments were conducted for this metal.

The results for nickel corrosion in SO_2 -argon mixtures can be summarized as follows. During the initial stages of reaction a porous oxide layer forms. SO_2 diffuses down the pores to the oxide/metal interface, where the oxygen activity is low enough so that nickel sulfide is thermodynamically stable. Nickel sulfide then forms as a thin layer between the metal and oxide and also grows into the pores of the oxide. A network of interconnected sulfides forms in the oxide matrix and acts as rapid diffusion paths for nickel

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to the scale/gas interface. These rapid diffusion paths account for the faster reaction rates in SO_2 than in O_2 . At the scale/gas interface the following reaction occurs:



Scale growth is initially linear, indicating that a surface step is rate controlling. However, during the later stages of reaction, scale growth obeys an apparent parabolic rate law, since diffusion of nickel outward is primarily rate controlling.

Other investigators have reported that cobalt reacts with SO_2 similarly to nickel (3-10). However, there are still many questions about the details of the reaction mechanism. Among the earliest investigations is that of Konev et al. (4), who exposed nickel and cobalt to CO_2 and SO_2 mixtures. For nickel, an outer layer of NiO and an inner layer of Ni_3S_2 were detected. However, for cobalt only CoO was detected. Alcock et al. (5) exposed cobalt at 688°C to $2\text{SO}_2:\text{O}_2$ streams for 2 hr. They observed the metal with a thin layer of CoS , followed by a thick layer of CoO , followed by a thin layer of CoSO_4 . More recently, Singh and Birks (6) have studied cobalt corrosion in SO_2 -argon mixtures from 500° to 900°C . They observed a thin sulfide layer (Co_9S_8) adjacent to the metal followed by a mixed oxide-sulfide layer ($\text{CoO-Co}_9\text{S}_8$), and they proposed that the inner sulfide layer forms by penetration of SO_2 into a porous oxide layer--a mechanism similar to that observed for nickel. Holthe and Kofstad (7) have also studied cobalt corrosion in SO_2 from 800° to 1000°C at 10, 100, and 760 torr. They also see duplex scales of oxides and sulfides. Although tests for sulfate are inconclusive, they suggest a very thin layer of sulfate may form on the oxide surface. Gesmundo and DeAsmundis (8) have studied cobalt corrosion in one atmosphere SO_2 from 450° to 1200°C . At 600° and 700°C they report approximate parabolic kinetics with increasing deviations at higher temperatures. Finally Gillot and Garnier (9) have examined cobalt corrosion in SO_2 from 450° to 1200°C at various SO_2 pressures. Generally at low temperatures they see parabolic kinetics and at higher temperatures linear kinetics. In summary, previous investigators agree that the reaction of cobalt and SO_2 leads primarily to cobalt sulfide and cobalt oxide. However the kinetics of the reaction are still not clear.

In this work, measurements were taken from 650° to 800°C --below the cobalt-sulfur eutectic. Particular attention was paid the effect of flow rates and the time dependence of scale growth in order to determine which step is rate limiting and to understand the mechanism of this reaction.

EXPERIMENTAL

High purity (99.999-percent pure) cobalt sheet was obtained from Johnson Matthey Chemicals, Ltd. Metallic impurities detected were Si-3 ppm and Al, Ca, Cu, Fe, Mg, Ag (each) < 1 ppm. This sheet was cut into rectangular specimens roughly $15 \times 10 \times 1\text{ mm}$. All samples were ground to 600 grit on SiC papers. Most of the samples were further polished to $.05\text{ }\mu$ on alumina wheels. This final polishing step had no major effect on the kinetics of the reaction or morphology of the product layer. However, $0.05\text{ }\mu$ polishing did

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give better reproducibility between runs--particularly at the lower temperatures. After polishing, sample dimensions were measured, and the sample was cleaned in xylenes and acetone.

A diagram of the experimental apparatus is shown in figure 1. Weight gains were measured with a Sartorius model 4104 balance, which had an accuracy of $\pm .06 \text{ mg/cm}^2$ in this system. The output of the balance was connected to a microprocessor with a crystal controlled clock which was set to transmit weight gains to a printer at one minute intervals. The sample was heated by a Hoskins alloy wound furnace, controlled to $\pm 1^\circ \text{ C}$ by an ECS model 6823 controller. This furnace was mounted on tracks for ease in loading and removing the sample. Sulfur dioxide-argon gas mixtures enter from the bottom of the quartz reaction tube. Note the presence of a porous alumina ceramic directly below the sample to bring the temperature of the reaction gas up to that of the sample. In order to prevent the hot sulfur dioxide from entering the balance mechanism, a counterstream of argon was passed through the top of the balance. All gases were dried over drierite; argon was also deoxygenated over BASF copper catalyst (150° to 200° C) or titanium sponge (700° C). Flow rates were controlled and monitored with Tylan model FC-260 mass flow controllers.

One concern with this type of apparatus is the possibility of forming a thin oxide layer during specimen loading and thermal equilibration. In order to avoid this, the following procedure was employed. With the furnace at room temperature, the sample was loaded into the reaction tube. Next the system was evacuated to better than .02 torr and backfilled with a 5 percent H_2/Ar mixture. This mixture was passed over the sample during furnace heat-up. After about 1/2 hr, the furnace was slid over the sample and allowed to come to thermal equilibrium for about 2 hr. Then the flow of argon was stopped and the system flushed with gettered argon for several minutes. After this, the flow of argon was stopped and the SO_2 -argon mixture admitted to begin a run.

After a run, the furnace was lowered and the specimen rapidly cooled. The reaction gases were stopped and replaced with a stream of gettered argon. When the furnace had cooled to room temperature the sample was removed from the reaction tube. Phases present were determined with X-ray diffraction and scale morphology examined with a scanning electron microscope. In order to examine scale cross sections, a $\sim 1 \text{ mm}$ thick layer of copper was electroplated on the sample from a copper sulfate solution. The plated sample was mounted and polished to 1μ with diamond paste. Samples had to be very gently polished to avoid separation at the scale/metal interface.

RESULTS

Figures 2 to 5 show kinetic results for 650° , 700° , 750° , and 800° C . Six to eight runs were performed at each temperature--the rate constants and final weight gains agreed to ± 10 percent. Flow rates were chosen so that gas-phase diffusion was not rate limiting (11). For each temperature, experiments were done at linear flow rates of 40.7 cm/min and 61.1 cm/min . These had little influence on the reaction rates, confirming that boundary layer gas-phase diffusion was not rate limiting under these conditions.

The three lower temperature reactions exhibit parabolic regions of different duration. At 650° C the sample reacts rapidly for the first 5 min. and then reacts according to a slow parabolic rate for the next 2 hr. At 700° and 750° C the sample follows a parabolic rate from the beginning of the reaction, with rate constants of 2.91 ± 0.31 and $7.18 \pm 0.44 \text{ mg}^2/\text{cm}^4\text{-min}$ respectively. This is shown in figure 4. Note that after 30 min at 700° C and 60 min at 750° C, the parabolic rates tend to decrease. At 800° C the sample reacts rapidly according to a linear rate law ($K_L = 1.2 \pm 0.1 \text{ mg}/\text{cm}^2\text{-min}$) for about 30 min. After this, the sample reacts quite slowly.

All four temperatures produced the same product phases: CoO-Co₉S₈-CoS. Some investigators have reported only CoO and Co₉S₈ (6,8, and 9). It is possible that in their cases CoS decomposed on cooling, since it is unstable below 460° C. Samples run at each temperature were checked for sulfate with X-ray diffraction and a method based on the higher solubility of CoSO₄ in water than cobalt sulfides and oxides (12). The samples were placed in 5 ml distilled water for several minutes and the water was checked for cobalt cations with an atomic absorption spectrometer. The concentration of cobalt cations for all samples was less than 1 ppm, which is the limit of resolution of the instrument. Thus there was no detectable sulfate layer on the surface of samples run under these conditions.

The morphology of the reaction product varied with temperature. At 650° C the scale consisted of a fine grained inner scale of sulfide and oxide and a coarse grained outer scale of sulfide and oxide. The fine grained scale which developed during the rapid reaction stage is shown in figures 6 and 8. There is no evidence of an inner pure sulfide layer adjacent to the metal. This type of morphology has been reported by other investigators (8).

At 700°, 750°, and 850° C a morphology similar to that for nickel at 600° C is observed. There is a thin sulfide band adjacent to the metal, followed by a duplex sulfide-oxide layer. This morphology develops with the first few minutes of reaction. Figure 11 shows a cross section of a sample run at 750° C for 2 hr. The darker areas are the sulfide and the gray area is the oxide matrix. The sample consists of a 1 μ thick sulfide layer adjacent to the metal followed by an oxide matrix with a fairly even distribution of sulfide. This sulfide band and sulfide distribution was evident in samples run at the three higher temperatures. Four point resistivity measurements gave very low values (~0.5 ohm-cm), indicating that the sulfides are interconnected. Sulfides have a higher electrical conductivity than oxides and therefore an interconnected sulfide structure should give these low resistivity values.

DISCUSSION

Figure 12 shows the cobalt stability diagram as a function of oxygen and sulfur potentials at 650° C (13, 14). Also shown is a line indicating the sulfur and oxygen potentials due to SO₂ dissociation. It is likely that the oxygen content of the system is 1 ppm or higher, due to manufacturer's reported oxygen impurities in the reaction gas. Figure 12 shows that under 0.1 atm SO₂ and 1 ppm O₂, cobalt sulfate is the stable phase. This is also true at 700° C. A similar situation exists for nickel at 600° C (1, 2). At 750°

and 800° C, cobalt oxide is stable under 0.1 atm SO₂ and 1 ppm O₂. As indicated in figure 12 cobalt sulfide is thermodynamically stable at the oxygen potential that must exist near the scale-metal interior.

The accepted theory of formation of an inner sulfide layer (1,2, and 6) is based on the initial formation of a porous metal oxide. SO₂ penetrates this oxide through the micropores and reacts to form sulfide at the oxide/metal interface where the oxygen potential is low. This process very likely occurs in the reaction of cobalt and SO₂, since the inner sulfide layer forms in the first few minutes of reaction. However, it is still not clear how sulfide forms at or near the scale/gas interface. Some investigators have proposed that sulfide forms via a sulfate intermediate, which exists at the scale/gas interface (15). However sulfate is stable only at the lower temperatures (650° and 700° C) and a sulfate layer has not been detected. Figures 8, 9, and 10 show a cross section of a sample reacted at 650° C and the large sulfide flames that project into the gas phase. Thus one must conclude that the scale does not equilibrate with the gas.

Before discussing the kinetics of the reaction of cobalt and SO₂, it is necessary to examine previous work on cobalt sulfidation (16 to 18). When cobalt reacts with 1 atm sulfur vapor, an inner Co₉S₈ layer forms and an outer CoS layer forms. Inert markers are observed between the two layers, suggesting that sulfur moves inward to form Co₉S₈ and cobalt moves outward to form CoS (16). From 500° to 750° C, cobalt reacts with sulfur vapor according to a parabolic rate law (17). It has been suggested that the diffusion of cobalt outward is rate limiting (18). Based on this, diffusivity of cobalt in CoS can be calculated.

In a previous paper (1), it was shown that the parabolic rate constant is related to the metal ion diffusivity by the following expression:

$$k_p = -2 D_{Co} c_{Co} \frac{\alpha f}{\beta \gamma} \Delta \ln a_{Co} \quad (2)$$

Here k_p is the parabolic rate constant (gm-cm⁻²-sec⁻¹), D_{Co} is the diffusion coefficient of cobalt in CoS (cm²-sec⁻¹), c_{Co} is the concentration of cobalt in CoS (gm-cm⁻³), f is the volume fraction of CoS ($f = 1$ for a single phase), and β and γ are conversion factors which relate the emerging flux of cobalt to weight gain. α is a factor based on the distribution of sulfide. For a single phase or an evenly distributed phase in an oxide matrix, $\alpha = 1$; for isolated islands of sulfide in an oxide matrix, $\alpha = 0$; and for an uneven distribution of sulfide in an oxide matrix, $1 > \alpha > 0$. Using the density of CoS (19): $\beta = 1.84$, $\gamma = 0.52$ cm³-gm⁻¹, and $c_{Co} = 3.53$ gm-cm⁻³. The activity gradient can be calculated from the cobalt activity at the Co₉S₈/CoS interface and the cobalt activity at the scale/gas interface. The latter is set by:



Table 1 lists the values of $D_{Co}(CoS)$ at each of the temperatures used in this study. Also shown are $D_{Co}(CoO)$ in 1 atm oxygen (20) which are several orders of magnitude lower than $D_{Co}(CoS)$. The values of $D_{Co}(CoO)$ are for diffusion in a single crystal; however, they are within 10 percent of those

calculated from oxidation of polycrystalline specimens (21). Given this kinetic background, the experimental results for the reaction of cobalt in sulfidizing-oxidizing environments can be discussed.

At 650° C, the reaction of cobalt with SO₂ is complex with two reaction stages, as shown in figure 2. During the first few minutes of reaction, a fine grain structure develops with many sulfides poking out of the oxide matrix. These sulfides are the light areas shown in figure 6. However, in only a few minutes time, many of these sulfides are severed and those that remain grow into large grains, as shown in figure 7. This is also evident in the cross section shown in figure 8--the bottom portion, which grew first, shows a coarse distribution. This explains the two reaction stages--initially cobalt diffuses out of the many available sulfide paths and the reaction is rapid; then some sulfide paths are severed the reaction rates decrease.

At 700° and 750° C, there appears to be one parabolic reaction stage. As mentioned, conductivity measurements indicate the sulfides are interconnected and fairly evenly distributed (figs. 8 and 13) in the oxide matrix. Thus equation (2) can be applied and the diffusivity of cobalt in CoS can be calculated from the measured parabolic rate constants. These diffusivities can then be compared to those calculated from the data of Mrowec and Werber (17). To apply equation (2) to the data presented here-- $\alpha = 1$, $\beta = 2.76$, and $\gamma = 0.62 \text{ cm}^3\text{-gm}^{-1}$. The volume fraction of sulfide was estimated by placing a grid over figure 13 and determining what fraction of the area was occupied by sulfide. This gave a value of 0.40, in agreement with the value of 0.42 obtained from the stoichiometry of the reaction:



The change in cobalt activity can be estimated by the difference between the cobalt activity at the Co₉S₈/CoS interface and the cobalt activity at the gas/scale interface, which is set by equation (4). The values of $D_{\text{Co}}(\text{CoS})$ calculated from the reaction of cobalt and SO₂ are listed in table 1. The agreement with the values calculated from Mrowec and Werber's sulfidation data is reasonable, indicating that under these conditions the diffusion of cobalt outward through the interconnected sulfides is primarily rate limiting. As mentioned previously, both the 700° and 750° C parabolic plots (fig. 5) show slower parabolic rates after 30 and 60 min, respectively. This is presumably due to a changing distribution of sulfide in the oxide matrix as shown in figures 13 and 14. Figure 13 shows a portion of the scale which grew during the first hour at 750° C (note the fairly even distribution of sulfide, indicating $\alpha = 1$). Figure 14 shows a portion of the scale which grew after 1 hr; the sulfide is now unevenly distributed, so $\alpha < 1$ which results in a slower parabolic rate.

At 800° C, the reaction initially shows a rapid linear rate and then slows dramatically after about 40 min. The linear rates suggest that cobalt diffusion outward is so rapid that an interfacial reaction becomes rate limiting. This interfacial reaction is very likely controlled by the rate of dissociation of SO₂.

The slow reaction stage is more difficult to interpret. When a sample which had reacted for 2 hr at 800° C was cooled, the scale separated at the sulfide layer-duplex layer interface. Figure 15 shows the portion of the

duplex layer which was adjacent to the sulfide layer. Note there are voids where there were once sulfides--only the oxide matrix is shown. It is possible that this void formation limits the outward diffusion of cobalt and slows the reaction.

CONCLUSIONS

In the reaction of cobalt with SO_2 at 650° to 800° C, the rapid diffusion of cobalt outward through an interconnected sulfide phase is important. The different kinetic behavior observed in this temperature range is due both to the increasing diffusivity of cobalt and differing morphologies of the sulfide phase. At 650° C the rates are initially rapid due to many available sulfide channels. After about 5 min the rates decrease due to a decreased number of sulfide channels. At 700° and 750° C diffusion of cobalt through these sulfides is primarily rate limiting and the $D_{\text{Co}}(\text{CoS})$ calculated compares favorably with that from previous sulfidation data. At 800° C diffusion through the sulfides is so fast that an interfacial step becomes rate limiting.

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TABLE 1. - DIFFUSIVITIES OF COBALT IN CoO AND CoS

Temperature, °C	$D_{\text{Co}}(\text{CoO})$, ref. 21	$D_{\text{Co}}(\text{CoS})$	
		Ref. 18	This work
650	1.45×10^{-11}	3.9×10^{-9}	----
700	3.82×10^{-11}	9.8×10^{-9}	2.2×10^{-8}
750	9.15×10^{-11}	2.7×10^{-8}	4.2×10^{-8}
800	2.02×10^{-10}	4.6×10^{-8}	----

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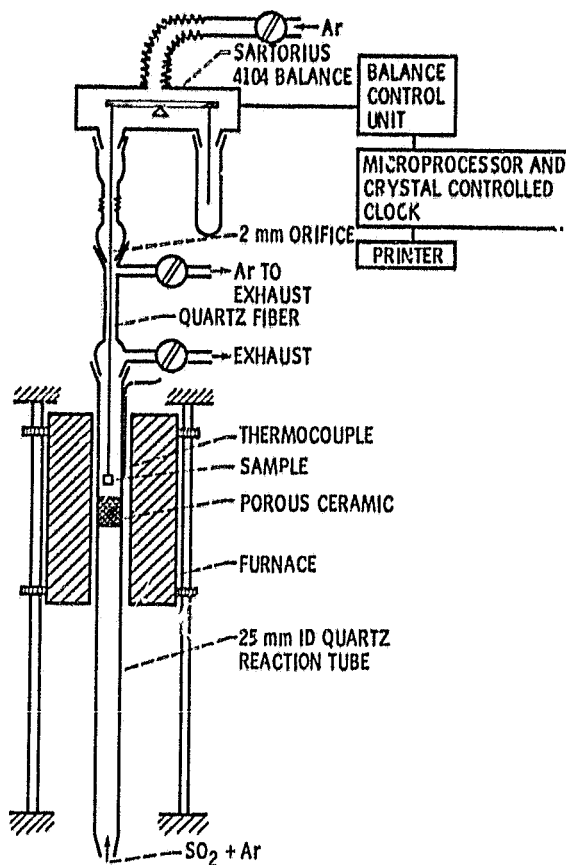


Figure 1. - Schematic of experimental apparatus.

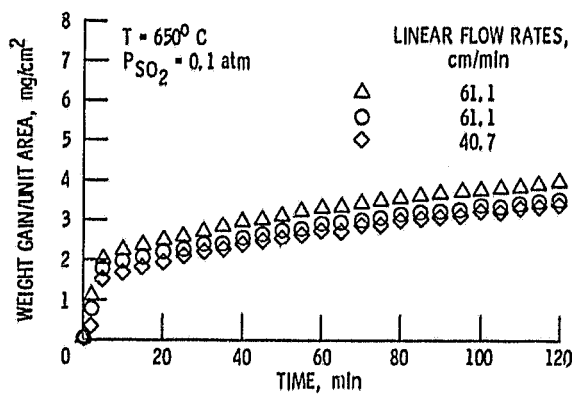


Figure 2. - Reaction of cobalt with SO₂ at 650° C.

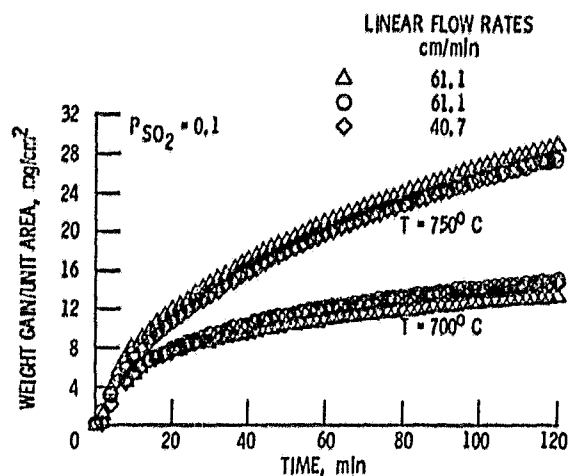


Figure 3. - Reaction of cobalt with SO_2 at 700 and 750°C.

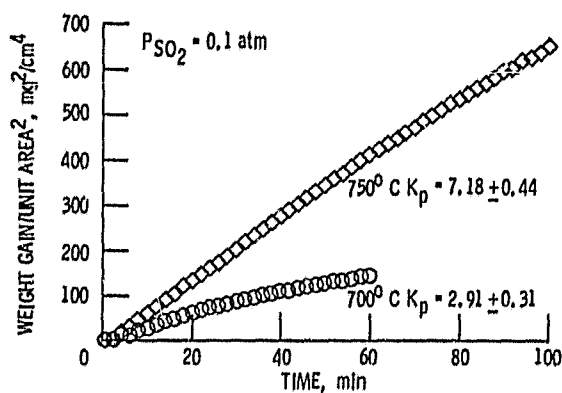


Figure 4. - Parabolic plot of Figure 3.

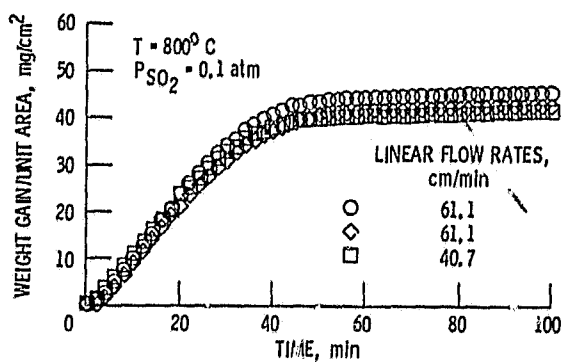


Figure 5. - Reaction of cobalt with SO_2 at 800°C.

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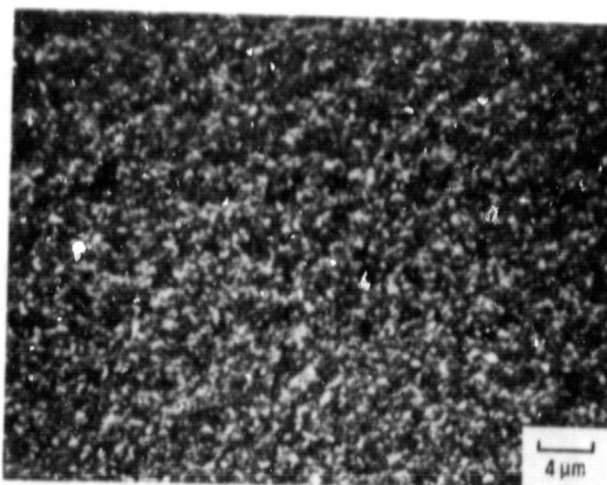


Figure 6. - Surface of a sample reacted for 3 minutes in 10% SO_2 -argon at 650°C . The light areas are the sulfide, the dark areas are the oxide.

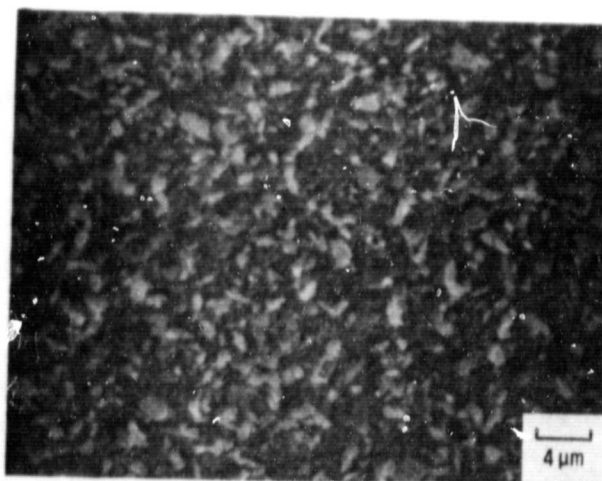


Figure 7. - Surface of a sample reacted for 5 minutes in 10% SO_2 -argon at 650°C . There are less sulfides and those that remain have become larger.

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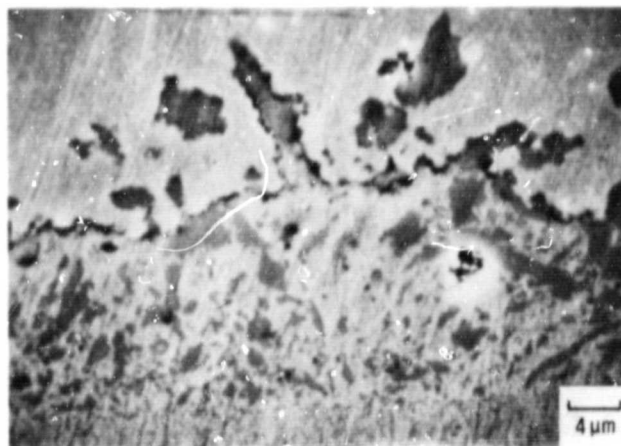


Figure 8. - Cross section of a sample reacted for two hours at 690°C for 2 hours. Note the fine grained structure at the bottom which was adjacent to the metal.

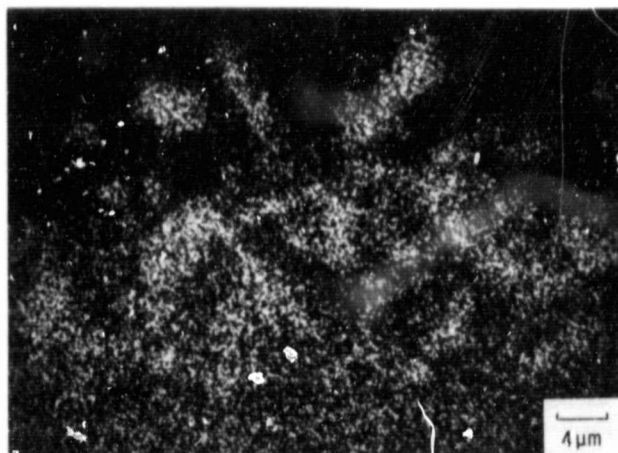


Figure 9. - Sulfur map of figure 8. Note the sulfide flames projecting into the gas phase.

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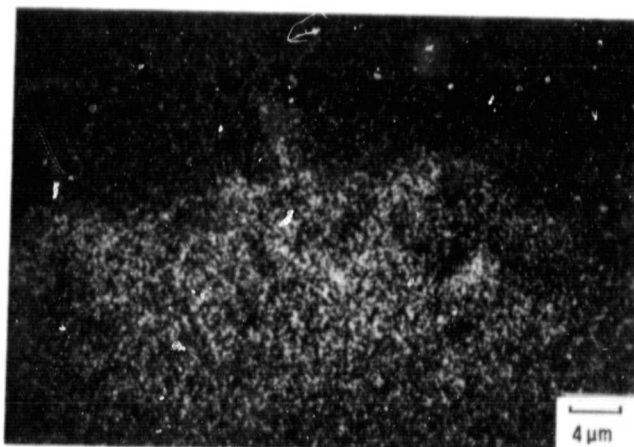


Figure 10. - Oxygen map of figure 8.

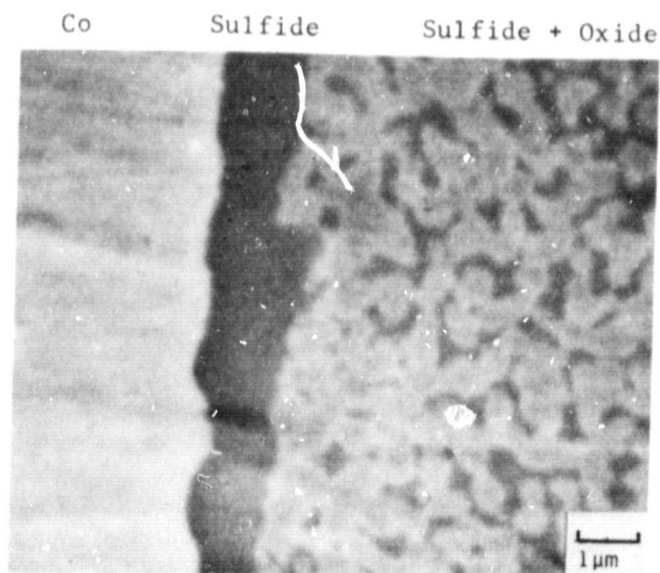


Figure 11. - Cross section of a sample reacted for two hours at 750°C.
The sulfide is the darker area.

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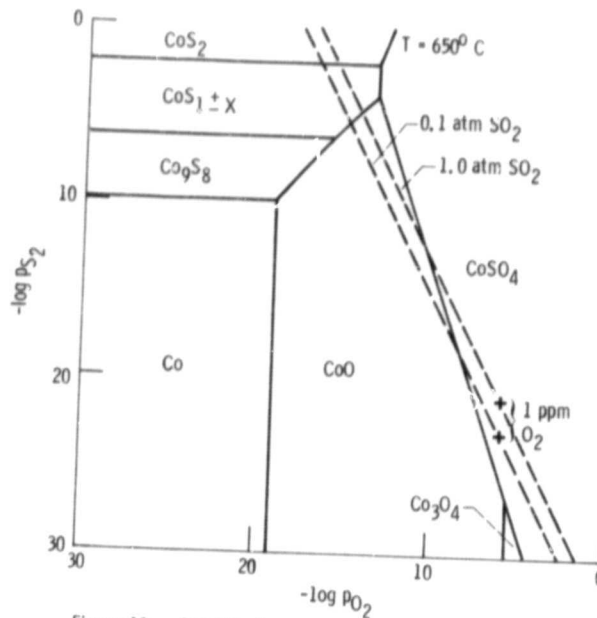


Figure 12. - Stability diagram of cobalt in a sulfur-oxygen atmosphere at 650°C .

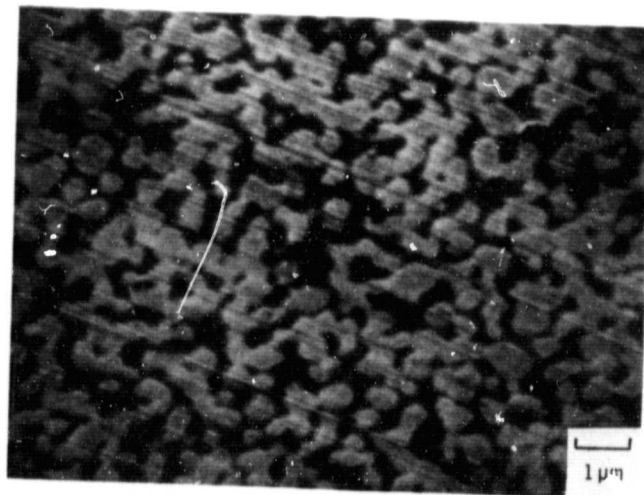


Figure 13. - Inner portion of duplex region of a sample reacted at 750°C for 2 hours. Note the even sulfide distribution.

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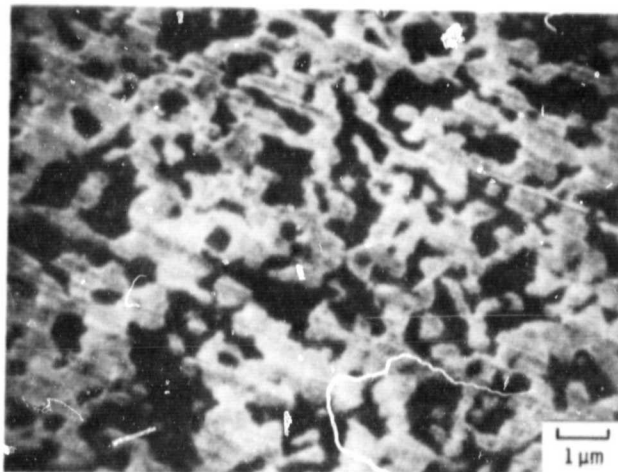


Figure 14. - Outer portion of duplex region of a sample reacted at 750°C for 2 hours. Note the uneven sulfide distribution.

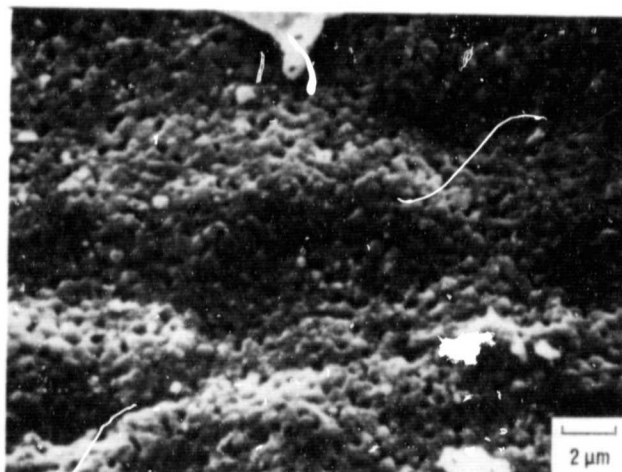


Figure 15. - Underside of a scale formed in 2 hours at 800°C. This is an oxide matrix and the voids are areas where there was once sulfide.